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Purification technologies for crude biodiesel obtained by alkali-catalyzed transesterification

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For commercial application, the ester product of alkali-catalyzed transesterification of vegetable oil or animal fats should be refined after glycerol separation by settling to fulfill the biodiesel standard specifications. This crude biodiesel, after neutralization and methanol removal, should be further cleaned by either one of the following methods: wet washing, dry washing, membrane extraction or using ion liquids. This paper presents a review on the traditional (wet and dry washing) and novel (membrane separation technology and usage of ion liquids) methods of crude biodiesel purification. It also provides a comparison of crude biodiesel purification methods. Each method has its advantages and disadvantages, which should be carefully analyzed when choosing the proper one for refining crude biodiesel.

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1. Introduction

Biodiesel, which usually refers to fatty acid methyl esters, is a notable environmentally friendly alternative fuel for diesel engines. It is commonly produced at commercial scale by alkali-catalyzed transesterification of vegetable oil and animal fats with methanol. Once produced, the mixture of fatty acid methyl esters (crude biodiesel) should be purified to comply with the specifications prescribed by the corresponding biodiesel standard such as EN 14214 or ASTM D6751. The downstream purification steps are needed to remove various impurities (unconverted triacylglycerols, monoacylglycerols, diacylglycerols, free fatty acids, glycerol, water, catalyst, soaps and others) from crude biodiesel to prevent a significant damage of diesel engines. Therefore, these processing steps are among the most important ones for commercial biodiesel production.

In the present work, the methods for purification of crude biodiesel produced by alkali-transesterification of various feedstocks are critically reviewed. At first, the conventional process of the biodiesel production is shortly described, paying attention to the main processing steps. Then, the effects of present impurities on the biodiesel quality are pointed out. The main part of this review paper deals with the traditional (wet and dry washing) and novel (membrane separation technology and use of ion liquids) purification methods. Finally, different methods of crude biodiesel purification are compared.

1.1. Biodiesel production process

There are many possible technological solutions for the biodiesel production from refined vegetable oils using alkali-transesterification reaction that it is difficult to describe them all in detail. Most of them are based on the block diagram shown in Fig. 1. The main stages of the biodiesel production process are as follows: (a) transesterification reaction, (b) separation of crude biodiesel from crude glycerol phase, (c) separation of biodiesel from wastewater and (d) drying of biodiesel. The process also involves the processing of the crude glycerol phase through (a) acidification and (b) separation of glycerol from alcohol. The biodiesel production process is further briefly described.

The alkali-catalyzed transesterification of vegetable oils using methanol or ethanol is the most commonly employed reaction for the biodiesel production at commercial scale. Sodium and potassium hydroxide or alcoxide are usually used to catalyze the transesterification reaction, sodium methoxide being most frequently applied. Alcohol is used in excess in order to shift this reversible reaction toward the formation of esters and glycerol. The most often molar ratio of methanol to vegetable oil is 6:1. The reaction is usually conducted at the temperature close to the boiling temperature of alcohol. The reaction time is relatively short since the conversion rate changes rapidly at the very beginning of the reaction. Batch and continuous stirred reactors are mainly used in industrial plants with agitation of the reaction mixture. As a rule, a higher conversion of vegetable oil gives the biodiesel of better quality. The final reaction mixture contains esters and glycerol as the main products, as well as mono-, di- and triacylglycerols, catalyst and soaps.

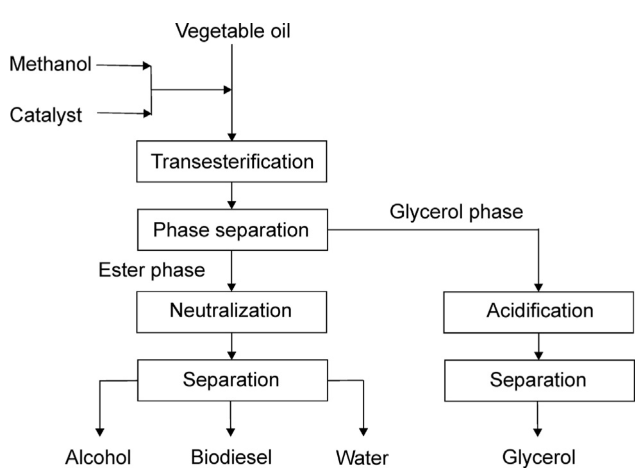


Fig. 1. Block diagram of the biodiesel production process.

After the transesterification reaction, crude biodiesel is separated from the glycerol phase. Since the solubility of glycerol in esters is low and the difference in density of the two phases is high enough (crude biodiesel 880 kg/m^3 and the glycerol phase 1050 kg/m^3), the separation of the two phases is relatively fast. The reaction mixture easily forms an emulsion at the interface between crude biodiesel and glycerol phase, especially in the presence of water. If the emulsion layer is not recovered, some of the products might be lost. The separation rate depends on the pH value of the reaction mixture and the presence of methanol. This separation is faster if the pH value of the reaction mixture is close to 7. Methanol is present in both phases and increases the solubility of glycerol and esters, slowing down the separation. Despite this negative influence on the separation rate, methanol is not usually recovered from the reaction mixture before separating crude biodiesel and the glycerol phase in order to prevent the undesirable glycerolysis of esters. At a small scale, the separation can be performed gravitationally in the transesterification reactor or a separate sedimentation tank. In the case of the continuous biodiesel production process at industrial scale, the separation is most often done with the help of disk centrifuges.

After being separated, crude biodiesel is neutralized by adding a mineral acid. Acidification will also help in removing any soap present in crude biodiesel. If potassium hydroxide is used as a catalyst, phosphoric acid is used to form potassium phosphate (K_3PO_4), which can be employed as a fertilizer. If sodium hydroxide or methoxide is used, then sulfuric or hydrochloric acids can be used in the neutralization stage, forming waste salts. In these cases, citric acid powder can also be used for the neutralization. In the case of water washing, the neutralization is a part of the biodiesel washing process and reduces the washing water consumption.

After the neutralization stage, there can be an intermediate stage of methanol separation from crude biodiesel. This separation is usually done as stripping, vacuum flash vaporization or falling film evaporation. If soaps are present in a considerable amount (>1000 ppm), crude biodiesel must be acidified to remove any soaps, which can cause foaming during the flash vaporization.

Crude biodiesel still contains some impurities such as acylglycerols, free fatty acids, methanol (if not recovered in the previous stage) and salts, which should be removed. Usually, water washing is used, although dry washing is also applied at commercial scale. Hot water (50–60 °C), which can be slightly acidified by a mineral acid, is used for the washing of crude biodiesel. In this way, salts and traces of residual glycerol and methanol are removed, while acylglycerols and free fatty acids remain in the biodiesel. Wastewater from the washing stage is separated from the biodiesel phase in a gravitational separator or through a centrifuge. The biodiesel is again washed with water which must be separated in the subsequent separation stage. Finally, the biodiesel is dried to eliminate the traces of water and get biodiesel fulfilling legal requirements. Drying can be carried out by flash or thin-film evaporation, commonly under vacuum, or by adsorption onto appropriate adsorbent materials followed by a filtration.

Biodiesel wastewater generated in the water washing process must be adequately treated before reuse or disposal [1]. In some cases, the recovery of methanol by distillation precedes the biodiesel wastewater treatment.

The glycerol phase, separated from crude biodiesel, contains mainly glycerol (50–60%), methanol, water, the catalyst and soap [2]. Usually, a mineral acid is added to the glycerol phase to convert the present soaps into insoluble free fatty acids and soluble salts. The free fatty acids are separated on the surface of the glycerol–methanol phase and can be reused in the esterification process.

Crude glycerol and methanol are usually recovered from the glycerol–methanol phase by vacuum flash evaporation. The crude glycerol contains about 85% of glycerol and can be further purified by vacuum distillation to get a product with at least 95.5% of glycerol or even with more than 99.5% of glycerol for pharmaceutical use. Methanol from refining stages of the biodiesel production process draws nearly the entire amount of water entering or being formed in the process. Using a distillation column, it is possible to separate methanol from the present water. The recovered methanol can be reused in the process if it has the water content less than 0.1%.

1.2. Effects of impurities on biodiesel quality

The performances of biodiesel as a fuel for diesel engines depend on its purity [3]. No, or minimal presence of impurities in the final product is the aim of each commercial production of biodiesel. Possible main impurities of biodiesel are glycerol, methanol, catalyst, acylglycerols, soap and salts. The impurities reduce the biodiesel quality and influence the engine performance through a number of negative effects [4,5]. When present in biodiesel, methanol reduces viscosity, density and flash point, deteriorates natural rubber seals and gaskets and corrodes parts of aluminum and zinc. Water reduces the heat of combustion, hydrolyzes a part of produced methyl esters, enables the bacteriological growth causing the blockage of filters, forms ice crystals resulting to gelling of fuels and corrodes fuel tubes and injector pumps. Also, water can cause the failure of the fuel pump and pitting in the pistons. The presence of soap (catalyst) damages the injectors and causes corrosion problems in the engine, filter plugging and the weakening of the engine. The oxidation stability of biodiesel is lower because of the presence of free fatty acids, which can also promote corrosion of the engine components. Acylglycerols can cause crystallization, turbidity, higher viscosity and deposit formation at pistons, valves and injection nozzles. Glycerol has several negative effects on biodiesel and engines such as the storage problem, settling problems, fuel tank bottom deposits, injector fouling, higher emission of aldehydes and acrolein and the engine durability problem.

The standards such as EN 14214 and ASTM D6751 show the correct chemical composition of biodiesel. Biodiesel producers tend to produce biodiesel with the quality indicators satisfying those prescribed by the standards. Glycerol is largely recovered by gravitational separation or centrifugation, while methanol is often removed by flash evaporation. Since these processes are not efficient in the complete removal of glycerol and methanol, an additional purification is needed to get the final product meeting the standard limits.

2. Purification of crude biodiesel

In order to meet the prescribed standard specifications, crude biodiesel is purified by two methods: wet washing and dry washing. Until recently, water washing was the most common purification method. Nowadays, both methods are generally accepted and applied at commercial scale. Since recently, novel purification methods have been developed and tested, such as the membrane separation technology and the use of ion liquids, for refining crude biodiesel. Table 1 summarizes the advantages and disadvantages of dry and wet washing for easy comparison.

2.1. Wet washing

Wet washing of crude biodiesel in order to remove soluble impurities such as residual catalyst, methanol, soap and glycerol can be conducted by using deionized water, mineral acid and water and organic solvents and water. Before the wet washing step, the excess of alcohol is sometimes separated by distillation or evaporation. The washed biodiesel is then dried over sodium sulfate or molecular sieves followed by filtration or by stripping with a hot gas.

Because of their high solubility in water, glycerol and methanol are very effectively removed from crude biodiesel by water

Table 1
Advantages and disadvantages of dry and wet washing.

Purification method	Advantage	Disadvantage
Wet washing	Very simple and effective method of purifying biodiesel	Requires a large amount of water
	Very effective removal of glycerol and methanol	Requires the use of deionized water
	Successful removal of residual soluble compounds and soap	Possible formation of free fatty acids by hydrolysis of esters in the presence of water
	Possible very high biodiesel purity (99%)	Drying of washed product is required to remove the trace amount of water, increasing energy cost
	Possible use of aqueous solutions of acids	Possible stable emulsion formation in the presence of soaps that can cause loss of biodiesel yield
	Can be combined with an organic solvent for removing the hydrophobic compounds	It is a time-consuming process because of multiple washings, water/biodiesel separation and drying of biodiesel
	Little lower running costs than dry washing	Generates a large amount of wastewater that should be properly treated before disposal or reuse
		Requires washing and settling tanks occupying a large surface area
Dry washing	Much easier and less effort than wet washing	Purified biodiesels might not fulfill the standard specifications
	Drastic reduction of waste water	Separation of the Magnesol from the biodiesel by filtration is quite difficult
	Decreases the total time of production	As much glycerol as possible should be removed before the use of an ion exchange resin
	No risk of water in the fuel	Ion exchange resins do not remove methanol
	Both magnesium silicate and ion exchange resin are very effective at removing soap	Need extra equipment (columns and pumps)
	Allows for continuous operation	Little higher running costs than water washing
	Requires less space than wet washing	Regeneration of the spent ion-exchange resins is not recommended by suppliers, so the solution for the generated solid waste should be find
	Spent Magnesol can be used as compost or an animal feed additive	Lack of information about the chemical composition of ion-exchange resins

washing. This method is also successful in removing residual sodium compounds and soap resulting from raw materials having free fatty acids. The saponification reaction is undesirable, because it not only consumes the catalyst but also causes problems in phase separation due to the formation of a stable emulsion during water washing [6,7]. The amount of soap formed during ethanolysis is three or four times higher than that formed during methanolysis under similar reaction conditions [8]. Therefore, the washing method will require a large amount of water [9]. Depending upon the ethanol-to-oil ratio employed in the biodiesel production, the separation of the phases may not occur, so glycerol should be added [9,10] or excess ethanol must be evaporated [11] to promote the separation. Water washing has many advantages, but also it creates a number of problems, as it can be seen in Table 1.

2.1.1. Washing with deionized water

This is a traditional technology of purifying crude biodiesel following its separation from the glycerol phase. Usually, hot deionized water (50–60 °C) is used. Different amounts of deionized water are reported. Balat and Balat [12] reported the 5.5% of water (by volume) that was added to crude biodiesel while the emulsion was stirred for 5 min.

Gonzalo et al. [13] studied water washing of crude biodiesels obtained from rapeseed and used cooking oils via acid-catalyzed esterification followed by alkali-catalyzed transesterification. A single water washing step was conducted in a stirred reaction vessel within 30 min. The effects of the catalyst loading, water amount and temperature on acidity, viscosity as well as the contents of water, sodium and methanol were estimated by a 2^3 full factorial design with three replications at the center point. While the acylglycerols' content was not influenced by the washing conditions, methanol, sodium and glycerol were almost completely removed from the crude biodiesel. Viscosity, density and acidity were slightly influenced by the water washing. The water content in the product increased with increasing the washing temperature and with decreasing the washing water amount.

Coêlho et al. [14] purified the ethyl esters of castor oil by water washing at different temperatures (30 and 70 °C) and pH values (2 and 5) using a 2^3 full factorial design with two replications. Two catalysts, sodium and potassium hydroxide, were employed. In the first wash, the acidified water (25% of biodiesel mass) was added to crude biodiesel. The emulsion was stirred and left to stand until the separation of the phases. Twice the smaller amount of water was used in the next washing steps. The separation of the phases was separated by centrifugation (2000 rpm for 10 min). The water washing was considered to be completed when the biodiesel fraction was neutralized (pH 7). The most influential factor on the amount of washing water was pH, followed by interactions of catalyst with pH and temperature. The water amount increased with increasing the pH of the washing water from 2 to 5. The effects of temperature and catalyst type were found not to be statistically significant.

2.1.2. Washing with water and organic solvent

To get a purified biodiesel, Siler-Marinkovic and Tomasevic [15] treated a reaction mixture mainly consisted of methyl esters and glycerol obtained by *in situ* transesterification of sunflower oil catalyzed by sulfuric acid. This mixture was filtered, washed first with petroleum ether and then four times with water until the wastewater was neutral. The ester/ether phase was dried with sodium sulfate, filtered and evaporated to remove petroleum ether. The need for removing petroleum ether from the final product will increase the costs of the plant equipment and operation.

In another study, Tomasevic and Siler-Marinkovic [16] refined the crude biodiesel originating from used frying oil with the solution of citric acid in methanol (50%) followed by washing with hot water until the wastewater was neutral. Again, the ester phase was dried with sodium sulfate and filtered. The purified methyl esters satisfied standard specifications and could be used as fuel in diesel engines.

2.2. Dry washing

Dry washing removes contaminants from crude biodiesel by adsorption or passing crude biodiesel through a bed of ion-exchange resin. Most operating procedures for dry washing are developed by trial and error [17]. Different adsorbent materials are used for treating crude biodiesel, such as magnesium silicate (Magnesol), calcium magnesium silicate, and cheap biosorbents. The spent adsorbent can be disposed of to landfill or other uses might be invented [5]. Also, different types of ion-exchange resins are applied for waterless refining of crude biodiesel. Usually, small styrene beads coated with polar functional groups are employed. The suppliers of these ion-exchange resins do not recommend regeneration of the spent material. Therefore, the main drawback of dry washing is to find a solution for the generated solid waste. Although the method using Magnesol has a better effect on the removal of methanol than ion-exchange resins, the purified biodiesels from both processes might not fulfill the specifications of EN Standard [5]. Major advantages and disadvantages of dry washing are presented in Table 1.

Since there are only a few reports on the application of dry washing, little is really known about the performance of the adsorbents and the ion-exchange resins used for this purpose. There are at least four possible mechanisms active in removing both insoluble and soluble impurities from crude biodiesel [17]: filtration, adsorption, ion exchange and glycerol/soap interaction. Depending on the process conditions and the properties of the adsorbent, one or more mechanisms can be dominant in the removal of impurities.

Solid impurities, such as insoluble soaps and glycerol, are removed from crude biodiesel by a mechanical action in the form of surface or depth filtration. This removal is especially effective at low methanol levels that reduce the solubility of soaps and glycerol in the biodiesel.

Some soluble impurities can be removed by adsorption through physical or chemical action. Namely, the polar impurities become physically or chemically bonded to the polar surfaces of the adsorbent particles. Adsorption is the main mechanism for the removal of glycerol using ion-exchange resins. The glycerol-saturated ion-exchange resin is regenerated by washing with methanol.

Ion exchange means exchanging the metal ion from the impurity, for instance sodium or potassium ion of the soap, for an ion from the ion-exchange resin (hydrogen ion), causing the breakdown of the impurity and forming free fatty acid.

There is a strong affinity between soap and glycerol. When adsorbed onto the adsorbent, glycerol forms a layer coating the adsorbent particles. Soap molecules, entrapped into the glycerol layer, are removed from crude biodiesel.

2.2.1. Dry washing by adsorption process

Özgül-Yücel and Türkay [18] used rice hull ash and a commercial silica gel to purify methyl esters by adsorption of free fatty acids under atmospheric conditions. Both adsorbents reduced the content of free fatty acids in the product. However, silica gel was a better adsorbent than rice hull ash, resulting in the smaller loss of

methyl esters and similar levels of free fatty acids. The content of methyl esters in the final product increased with increasing the silica gel dosage.

Dmytryshyn et al. [19] also used silica gel for purifying biodiesels obtained by alkali transesterification of various feedstocks using methanol. At first, methanol was removed from the crude biodiesel by vacuum evaporation. Then, the biodiesel was stirred with silica gel for 20 min and filtered to remove the silica gel. Finally, the filtrate was passed through a bed of sodium sulfate to remove traces of water. The canola methyl ester had physical and chemical properties similar to diesel fuels. The acid value of the final products was below the specified limit.

Yori et al. [20] used fixed silica beds for removing glycerol from mixtures of glycerol and purified biodiesel. Fresh silica has a great glycerol adsorption capacity of 0.13 g/g, and the breakthrough of the bed depended on the feed rate, the concentration of glycerol and the mass of adsorbent. With the particles of 1–1.5 mm, the full adsorption capacity of the bed was used since the breakthrough and saturation points almost coincided. With greater silica beads (1/8 in), the breakthrough point was at about one-half of the time for full saturation because of internal mass transfer limitations. The silica bed could be regenerated by eluting with methanol (4 bed volumes) followed by drying in a nitrogen stream (1 h). The adsorption of glycerol was not affected by small amounts of water and soaps present in the biodiesel, while monoacylglycerols and methanol reduced the effective saturation capacity [21]. This method was successfully applied for refining the biodiesel obtained by a non-catalytic process [22].

Suppalakpanya et al. [23] added pure glycerol to the final reaction mixture from alkaline-catalyzed ethanolysis of crude palm oil, and the resulting mixture was heated in a microwave oven (70 W, 1 min). After separation by gravity, the ester layer was heated at 80 °C to remove excess ethanol, then treated with bleaching earth, mixed (5 min) and centrifuged. The optimum amounts of pure glycerol and bleaching earth were 10% and 1.2%, respectively reducing the residual glycerol content below the standard limit. The final product met the ASTM biodiesel standard.

Solval and Sathivel [24] studied the production of biodiesel from pollock oil by the NaOH-catalyzed methanolysis and the effect of the adsorption process on the properties of biodiesel. Activated bleaching earth was used as an adsorbent at the biodiesel-to-earth mass ratio of 1:10. The biodiesel obtained met the specifications stipulated by the ASTM biodiesel standard.

Sohling et al. [25] suggested the use of a natural clayey material (i.e. natural silica-smectite mixture) for the purification of crude biodiesel based on soybean oil. This adsorbent showed a good performance in removing free and total glycerol, which was comparable to that of a commercial synthetic magnesium silicate.

Leeruang and Pengprecha [26] showed that an activated low silica bentonite (120–200 mesh) was an efficient adsorbent for purifying biodiesel. The natural material was activated with 0.1 M sulfuric acid at 100 °C for 1 h. The adsorption isotherm was fitted with the Freundlich model. About 47% of glycerol could be removed by using 5% of activated bentonite.

2.2.2. Dry washing by ion-exchange process

Wall et al. [17] investigated the mechanisms governing the purification of biodiesel using ion-exchange resins. Three resins, T45BD, T45BDMP (Thermax) and BD 10Dry (Dow Chemical), were used in the form of fixed-bed columns. The models of crude biodiesel were prepared by clean biodiesel glycerol and alkali methoxide dissolved in methanol. The results confirmed four mechanisms for soap and glycerol removal: filtration, physical adsorption, ion exchange and soap removal by glycerol affinity. The sodium soap was more effectively filtered than the potassium one. The removal efficiency of sodium soap increased with decreasing the resin particle size, while the potassium soap removal was not influenced by the resin particle size. Ion-exchange resins reduced the soap level from 1200 ppm to below 50 ppm and the glycerol level from 0.08% to below 0.02% for 550 and 200 bed volumes of the treated biodiesel, respectively. Gel and macroporous resins had similar soap removal efficiency, and gel resins from different producers provided similar soap and glycerol removal efficiency.

Chen et al. [27] reported that glycerol in fatty acid methyl esters exhibited a great affinity to a sulfonated resin (sodium form). The best adsorption isotherm model was the Freundlich one. The adsorption process of glycerol onto the resin was physical, spontaneous and exothermic. However, the hydrogen form of the sulfonated adsorbent showed higher adsorption capacity for glycerol than its sodium form [28]. This adsorption was also physical and spontaneous but endothermic. Interactions between the glycerol molecules and the sulfonated resins were dominated by strong hydrogen bonding.

2.2.3. Coupled wet and dry washings

Baroutian et al. [29] employed a two-step purification method that combined wet and dry washings. In the first step, hot distilled water (60 °C) acidified with tannic acid (0.1%) was used to wash crude biodiesel. The mixture of crude biodiesel and the acidified water (volume ratio 2:1) was moderately stirred. This process was continued until the biodiesel phase became clear. The two phases were separated by gravity, and the biodiesel layer was dried at atmospheric conditions. With water washing, the catalyst content of the crude biodiesel was reduced from 44.32 mg KOH/kg to 5.74 mg KOH/kg. The second step involved the adsorption onto activated palm shell carbon. The suspension of activated carbon in the prewashed biodiesel was shaken at a controlled temperature. Adsorbent loading, time and temperature were optimized with respect to the catalyst (KOH) removal. Under the optimum adsorption conditions (0.9 g of activated carbon per 25 mL of biodiesel, 20 h and 40 °C), the catalyst removal of only 24% was achieved.

2.3. Novel methods of crude biodiesel purification

The removal of impurities from crude biodiesel may be achieved by using novel purification methods such as membrane separation and extraction by ionic liquids and deep eutectic solvents.

2.3.1. Membrane separation technology

Membrane based separations are well-known technologies used in water purification and protein separations. At present, these membrane technologies are commercially applied in separations of aqueous solutions, but the treatment of non-aqueous fluids by membrane separation is currently emerging. The membrane can be organic (i.e., polymeric) or inorganic in nature. Because of their chemical and thermal stabilities, the latter type, especially the ceramic membranes, is more suitable for using with organic solvents.

The membrane separation technology has already been used in the production and purification of biodiesel. Shuit et al. [30] have been recently reviewed the biodiesel production using the membrane reactor technology. This technology has been tested for separation of glycerol from biodiesel without previous settling [31,32]. When applied for biodiesel purification, this new method simplifies the separation steps and no, or little wastewater is generated. One disadvantage is that the ceramic membrane must be cleaned. Methanol removes the soap easily, and free glycerol accumulates on the surface and/or precipitates over the membrane pores [33]. Methanol should be purified for reuse in

Table 2
Comparison of different methods of crude biodiesel purification.

Reactants used in biodiesel production	Purification methods	Operating conditions of purification	Product properties[c]	Concluding remarks	Reference
Rapeseed oil, methanol, NaOH	Water washing: hot distilled water washing of crude biodiesel followed by drying with sodium sulfate[a]	Water-to-biodiesel 1:1; 50, 65, 80 °C; two washings without stirring and three washings with stirring	RY: 79.5–84.2; WC: 700–1600; AV: 0.47–0.57	The product biodiesels have approximately the same composition. Washing with hot distilled water at 50 °C was the best refining method (RY: 84.2%; WC: 0.07%; AV: 0.47 mg KOH/g)	[52]
	Wet washing: petroleum ether and distilled water washing of crude biodiesel, followed by water washing until neutral pH (adjusted by acetic acid), drying with sodium sulfate, filtering and evaporating under vacuum[b]	Petroleum ether-to-biodiesel-water: 1:1:2; 20 °C; three water washings	RY: 82.6; WC: 1400; AV: 0.78		
	Wet washing: neutralization of the reaction mixture with sulfuric acid (1:1) followed by centrifugation, gravitational separation of the ester phase vacuum evaporation and drying with sodium sulfate[b]	20 °C; pH 7	RY: 80.9; WC: 2200; AV: 6.08		
Animal fat and soybean oil (1:1 by vol.), methanol, sodium methoxide	Wet washing: neutralization with a solution of citric acid (1%), washing with a solution of sodium chloride (3%), washing with deionized water (three times) and dehydration with a molecular sieve[b]	–	RY: 81; WC: 321; AV: 0.16; EC: 91.2	Wet washing gave a better esters yield. Most of the product properties were almost identical; only the oxidative stability, the total contamination and the sulfur content were slightly better for the dry washing	[53]
	Dry washing: adsorption with Magnesol D60 (2%; 0.45 μm), settling overnight and filtering[b]	Stirring for 30 min; 77 °C	RY: 75; WC: 334; AV: 0.45; EC: 95.2		
Waste cooking (sunflower) oil, methanol, KOH (two-step process)	Wet washing[b]:			The product meets the standard criteria. Their properties correspond to the initial feedstock properties. The silica gel and phosphoric acid methods are more suitable for the purification of crude esters, ensuring the highest refining yield	[54]
	Hot distilled water (up to 10 times) until neutral pH, followed by drying over sodium sulfate	50 °C	RY: 89; WC: 1000–1200; AV: 0.23–0.80		
	Acidified water (5% phosphoric acid; up to seven times) until neutral pH, followed by drying over sodium sulfate[b]	50 °C	RY: 92; WC: 1000–1300; AV: 0.20–0.34		
	Dry washing: adsorption with silica gel, followed by drying over sodium sulfate[b]	Fixed bed	RY: 92; WC: 400–500; AV: 0.10–0.39		
Refined edible oil, methanol, sodium methoxide, waste cooking oil, methanol, KOH	Wet washing[a]: deionized water, tap water or acidified water (5% phosphoric acid)	Ester-to-water 1:1, 1:0.75 and 1:0.5; stirring (200 and 400 rpm) for 30 min; 22 and 60 °C	WC: 1050; AV: 0.18–0.22; MC: 0.04–0.07; FGC: 0.01	Similar results of purifying the biodiesels from different feedstocks are obtained with the applied methods. None of the methods affect significantly AV, oxidative stability, acylglycerols content or WC. Only wet washing purifies the esters to the standard requirements, reducing methanol and glycerol levels below the limits (excluding WC). The optimal conditions: ambient temperature, tap water, 200 rpm and water-to-ester ratio of 0.5:1	[5]
	Dry washing: adsorption with Magnesol (60 μm; 0.25–1.00%)[a]	Stirring for 30 min; 22 and 60 °C	WC: 1050; AV: 0.11–0.20; MC: 0.51–0.80; FGC: 0.03–0.04		
	Dry washing: adsorption with ion exchange resins (Amberlite BD10 Dry; Purolite PD 206)[a]	Fixed bed; 22 °C	WC: 1050; AV: 0.20–0.27; MC: 0.94–1.14; FGC: 0.03–0.04		
Waste animal fats (beef tallow, pork lard, chicken fat), methanol, KOH	Wet washing: neutralization with phosphoric acid, followed by distilled water washing until neutral pH, drying by adsorption in MgO and vacuum filtration[b]	85 °C	RY: 90.8, 91.4, 76.8[d]; WC: 374, 184, 1201; AV: 0.20, 0.22, 0.55; EC: 84.4, 80.7, 73.8	The products obtained by the two purification methods are similar in terms of the properties evaluated. However, none of the products have the EC satisfying the standard limit. Wet washing is very effective in removing contaminants, especially Group I metal (Na+K) and WC	[55]
	Dry washing: adsorption with ion exchange resin (Lewatit GF 202; 0.65 mm)[b]	Fixed bed	RY: 90.8, 91.4, 76.8; WC: 795, 114, 1273; AV: 0.21, 0.17, 0.09 mg; EC: 81.2, 83.0, 83.4		
Sunflower oil, ethanol, sodium methoxide (two-step process)	Wet washing[a]:			All methods are very effective in removing soap and free glycerol. The key step is neutral washing. Only this step reduces the AV below the standard limit. The advantage is the use of non-corrosive water saturated with carbon dioxide	[56]
	Washings with neutral water and water saturated with carbon dioxide	Water: 10% and 30% by vol. of the ester phase; stirring for 15 min; 60 °C	AV: 0.32; FGC: 0; SC: 0		
	Washings with acidified water (5% HCl) and water saturated with carbon dioxide		AV: 1.29; FGC: 0; SC: 0		

		Each washing with 30% by vol. of the ester phase; Stirring for 15 min; 60 °C			
	Dry washing: adsorption with ion exchange resin (Amberlite BD10 DRY) followed by stripping by nitrogen (80–100 °C)[b]	Fixed bed, 3 L/(kg h); 60 °C	AV: 1.36; FGC: 0; SC: 0		
Waste cooking oil, methanol, KOH (two-step process)	Wet washing: extraction with distilled water, tap water or glycerol, followed by centrifugation[a]	Extraction agent: 5, 10 and 15%, added in one or two steps; vigorously shaking for 10 min	WC: 1603, 1284, 253[e]; AV: 0.46, 0.43, 0.38; SC: 23.7, 79.4, 64.2; MC: 0.05, 0.04, 0.08; FGC: 0.002, 0.002, 0.020; EC: 92.1, 91.4, 91.8	All the methods can remove soap, methanol and glycerol effectively. None of the methods affects ester and glyceride content, but some of them influence water and free fatty acids content. The most suitable method is the two-step extraction using glycerol (15%)	[57]
	Dry washing: adsorption with magnesium silicate or bentonite, followed by centrifugation[a]	Adsorbent: 0.50–1.00%; stirring (200–600 rpm) for 15 min; 22 °C.	WC: 803, 809[f]; AV: 0.27, 0.22; SC: 33.8, 26.4; MC: 0.20, 0.27; FGC: 0.005, 0.008; EC: 90.9, 89.9		
	Dry washing: adsorption with ion exchange resin (Lewatit GF202)[a]	Fixed bed at 2 BV/h; 22 °C.	WC: 741; AV: 0.35; SC: 32.5; MC: 0.14; FGC: 0.008; EC: 91.5		
Soybean oil, methanol, KOH	Wet washing washing with acidified distilled water (2% by vol. phosphoric acid) followed by washings with hot distilled water	Water: 10% by vol.; stirring for 5 min; 55 °C	WC: 1400; AV: 0.22; SC: 158; MC: 0.18; FGC: 0.01	The adsorbents are more efficient in water and soap removal. Only Magnesol and wet washing reduce the MC below the limit level. The most efficient methods include Magnesol (1%) and silica (2%) that are also suitable for free and bonded glycerol removal	[58]
	Dry washing: adsorption with magnesium silicate (Magnesol) or silica[b]	Adsorbent: 1 or 2%; stirring for 20 min; 65 °C	WC: 500, 500[g]; AV: 0.17, 0.14; SC: 60.8, 60.8; MC: 0.19, 0.22; FGC: 0.02, 0.03		
	Dry washing: adsorption with ion exchange resins (Amberlite BD10 DRY; Purolite PD 206)[b]	Adsorbent: 1 or 2%; stirring for 20 min; 65 °C	WC: 900, 1100[h]; AV: 0.14, 0.21; SC: 183, 243; MC: 0.39, 0.59		
Waste cooking oil, methanol, KOH	Wet washing: extraction with 1% phosphoric acid, followed by hot water washing (twice) and heating (90 °C, 30 min)[a]	55 °C	WC: 3610; AV: 0.18; MC: 0.018; FGC: 0.0020	Rice husk ash (4%) shows similar results as Magnesol or acid solution. None of the methods is efficient in water removal	[59]
	Dry washing: adsorption with magnesium silicate (Magnesol), followed by filtration[a]	Adsorbent: 1%; stirring for 20 min; 65 °C	WC: 2023; AV: 0.29; MC <0.01; FGC: 0.0002%		
	Dry washing: adsorption with rice husk ash, followed by filtration[a]	Adsorbent: 1–5%; stirring for 20 min; 65 °C	WC: 1183[i]; AV: 0.15; MC <0.01; FGC: 0.0039		
Waste cooking oil, methanol, KOH	Water washing[b]	-	RY: 88; AV: 0.30	All the adsorbents result in higher refining yield than water washing and better fuel properties. The spent activated can be regenerated and reused	[60]
	Dry washing: adsorption with activated carbons from spent tea (activated thermally or by steam), regenerated spent activated carbon and silica gel[b]	Fixed bed	RY: 97, 94.5, 94, 93[j]; AV: 0.092, 0.144, 0.195, 0.247		
Sunflower oil, ethanol, sodium methoxide	Wet washing: extraction with aqueous solution of HCl (5%)[b]	90 °C	RY: 84.2; WC: 1260; AV: 3.10; FGC: 0; EtC: 0.02	Distillation is the best purification method. The final products meet most of the specified requirements. None of the method reduces the WC below the limit	[61]
	Dry washing: adsorption with silica (2%) and auxiliary filter celite (1.6%)[b]	Stirring for 30 min; 90 °C	RY: 84.6; WC: 788; AV: 0.93; FGC: 0; EtC: 0.02		
	Distillation[b]	Pressure: 680 mmHg	RY: 92.3; WC: 566; AV: 0.30; FGC: 0.02; EtC: 0.07		
Soybean oil, methanol, NaOH	Wet washing:			All the washing methods result in the products of a high purity are obtained by all the washing methods (97.5%) and the membrane extraction (>98%). None of the methods produce the product with WC below the limit, except the polyacrylonitrile membrane extraction	[62]
	Distilled water washing (three times) followed by drying over sodium sulfate and filtration	Ester-to-water: 1:1; stirring for 20 min; 20, 50, 80 °C	EL: 15.2, 10.1, 10.8[k]; WC: 1120, 560, 710; EC: 97,6, 98.0, 98.1		
	Neutralization with HCl (pH 1) followed by distilled water washing (twice), drying over sodium sulfate and filtration				

Table 2 (*continued*)

Reactants used in biodiesel production	Purification methods	Operating conditions of purification	Product properties[c]	Concluding remarks	Reference
		Ester-to-water: 1:1; stirring (125 or 150 rpm) for 20 min; 20 °C	EL: 12.4, 13.2[l]; WC: 540, 660; EC: 97.9, 97.9		
	Extraction with *n*-hexane or petroleum ether followed by distilled water washing (three times), drying over sodium sulfate and filtration	Ester-to-solvent: 1:1; stirring for 20 min; 20 °C	EL: 13.0, 13.6[m]; WC: 730, 710; EC: 97.6, 97.8		
	Hollow fiber membrane extraction (1 m long, 1 mm diameter) followed by drying over sodium sulfate and filtration	Flow rate: 0.5 mL/min at 0.1 MPa; 20 °C	EL: 8.1, 10.3[k]; WC: 420, 1070; EC: 98.5, 98.0[n]		

[a] After the separation of ester and glycerol phases.
[b] Following the separation of ester and glycerol phases, methanol in the ester phase was removed.
[c] RY, refining yield (%); WC, water content (mg/kg); AV, acid value (mg KOH/g); MC, methanol content (%); EtC, ethanol content (%); EC, ester content (%); FGC, free glycerol content (%); SC, soap content (%); EL, ester loss (%).
[d] Beef tallow, pork lard and chicken fat, respectively.
[e] Distilled water, tap water and glycerol, respectively; two steps.
[f] Magnesium silicate and bentonite, respectively.
[g] Magnesium silicate (1%) and silica (2%), respectively.
[h] Amberlite and Purolite, respectively at 2%.
[i] 4% rice husk ash.
[j] Activated carbon by steam, thermally activated carbon, regenerated spent activated carbon and silica gel, respectively.
[k] 20, 50 and 80 °C, respectively.
[l] 125 and 150 rpm, respectively.
[m] *n*-Hexane and petroleum ether, respectively.
[n] Polysulfone and polyacrylonitrile, respectively.

membrane cleaning. This membrane separation technology is environmentally friendly for refining of crude biodiesel. The drawbacks of this technology are the increase of the final biodiesel production cost and the decrease of throughput by possible contamination [34].

Wang et al. [33] used the membrane separation technology to purify the crude biodiesel produced from refined palm oil via alkali-catalyzed two-step transesterification. After removing methanol, the crude biodiesel was micro-filtered by the ceramic membrane to remove the residual glycerol, catalyst and soap. Three ceramic membranes with the pore size of 0.1, 0.2 and 0.6 μm were tested. At the transmembrane pressure and the temperature of 0.15 MPa and 60 °C respectively, the best results in removing free glycerol, sodium, potassium, calcium and magnesium were achieved with the 0.1 μm membrane. When the volumetric concentration ratio reached 4, under the same operating conditions, the flux through the membrane was 300 L/m^2 h (83.3% of the initial flux). The contents of free glycerol, potassium, sodium, calcium and magnesium in permeate were reduced to 0.0108%, 1.40 mg/kg, 1.78 mg/kg, 0.81 mg/kg and 0.20 mg/kg, respectively and were better than those of water washing.

Saleh et al. [35] employed ultrafiltration to remove free glycerol from biodiesel obtained by methanolysis of canola oil. A modified polyacrylonitrile membrane (100 kD cut-off) was used at 25 °C and 552 kPa. Low concentrations of water had a great positive effect on the removal of glycerol from the FAME, while the presence of methanol affected the glycerol separation negatively. The membrane technology used 2.0 g of water per liter of the treated biodiesel (0.225 mass% water), which was four orders of magnitude less than the amount of water required for the conventional water washing. The mechanism of free glycerol separation from biodiesel was due to the removal of an ultrafine dispersed glycerol-rich phase present in the untreated FAME. In a continuing study, Saleh et al. [36] tested a membrane separation system using ceramic membranes for the removal of glycerol from crude biodiesel at different temperatures. Ceramic membranes in the ultrafiltration (0.05 μm) and microfiltration (0.2 μm) ranges were employed. For faster glycerol separation, higher operating temperatures promoted reaching the appropriate concentration factor sooner. Moreover, the smaller pore size of the ultrafiltration membrane facilitated the glycerol removal compared to the microfiltration membrane. The ASTM standard for the free glycerol content and the concentration factor greater than 1.6 was met utilizing the ultrafiltration membrane at 25 °C after 3 h.

Using a ceramic membrane (pore size of 0.02 μm), Atadashi et al. [37] purified crude biodiesel to meet the biodiesel standard specifications. The use of acidified water was a key factor to the successful removal of glycerol and catalyst. The process parameters (transmembrane pressure, temperature and flow rate) significantly affect the separation process. However, the membrane performed better at moderate transmembrane pressures than at higher temperatures. The optimum operating conditions were as follows: a transmembrane pressure of 2 bar, a temperature of 40 °C and a flow rate of 150 L/min with permeate flux of 9.08 kg/m^2 h. The ceramic membrane retained its performance capabilities after several months of use.

2.3.2. *Ionic liquids in crude biodiesel purification*

Ionic liquids have recently attracted attention in the biodiesel production, where they can act as a catalyst, cosolvent or extracting solvent [38]. Chemically, they are organic salts with melting points around or below the ambient temperature, which are composed of organic cations and either organic or inorganic anions. They are an environmentally attractive alternative to volatile organic solvents because of their unique physico-chemical properties [39], such as

negligible vapor pressure, high chemical and thermal stability and the ability to dissolve a number of various compounds.

Because of the complexity of their synthesis and the high cost of starting chemicals, ionic liquids are replaced by so-called deep eutectic solvents which are formed from the mixture of organic halide salts with an organic compound. When these two components are mixed in a proper ratio, a eutectic point is observed. The organic compound, as a hydrogen-bond donor, forms a hydrogen bond with the halide ion. Considering that deep eutectic solvents contain a significant molecular component, the researchers show ambivalence on whether they could be formally classified as ion liquids. However, their properties as tunable solvents are comparable to those of ionic liquids. Furthermore, they have several advantages over ionic liquids, such as easy preparation in high purity at low cost, non-toxicity, no reactivity with water and biodegradability [40].

Ion liquids are used as an extracting solvent in the biodiesel production for extracting lipids from microalgae and oil seeds [41,42], free fatty acids from the oily feedstock [43], glycerol from the biodiesel product [44], as well as glycerol [45] and unsaturated fatty acid esters [46] from crude biodiesel.

Abott et al. [44] showed that a glycerol-based deep eutectic solvent is efficient in the separation of glycerol and biodiesel from the final reaction mixture obtained from rapeseed and soybean oils by ethanolysis in the presence of KOH. The most effective solvents contained quaternary ammonium salt and glycerol at a molar ratio of 1:1. The best glycerol removal was achieved using choline chloride, $[ClEtMe_3N]Cl$, and $[EtNH_3]Cl$. The amounts of glycerol remaining in the soybean and rapeseed biodiesels after separation using the 1:1 glycerol:choline chloride mixture were 0.06% and 0.02%, respectively.

Hayyan et al. [45] successfully used a quaternary ammonium–salt–glycerol-based deep eutectic solvent for the extraction of glycerol from crude biodiesel based on palm oil. The crude biodiesel contained 0.28% of total glycerol, which was higher than the standard limit. The best glycerol removal (51%) was achieved with the molar ratio of biodiesel to deep eutectic solvent of 1:1. In this case, the optimum composition of the deep eutectic solvent was 1:1 (salt:glycerol).

Shabaz et al. [47–49] have confirmed that deep eutectic solvents are effective in the removal of glycerol, mono- and diacylglycerols, as well as an alkali catalyst from crude biodiesel obtained from palm oil. The deep eutectic solvents were synthesized from choline chloride and methyltriphenylphosphunium bromide (MTPB) as a salt component and various hydrogen-bond donors. The mixtures of choline chloride with ethylene glycol (molar ratio of 1:2.5) or 2,2,2-trifluoroacetamide (molar ratio of 1:1.75) efficiently removed glycerol from crude biodiesel at the optimum molar ratio of deep eutectic solvent to biodiesel of 1:1 [47]. The deep eutectic solvents based on MTPB and ethylene glycol or triethylene glycol removed all free glycerol from crude biodiesel, while the total glycerol content was reduced below the standard limit [48]. Moreover, triethylene–glycol-based deep eutectic solvent (molar ratio of 1:4) removed mono- and diacylglycerols for 37.9% and 53.4% at the solvent-to-biodiesel molar ratio of 3:1 and 0.75:1, respectively. The same research group developed an artificial neural network model to predict the removal of glycerol from crude biodiesel using choline chloride- and MTPB-based deep eutectic solvents [50]. The deep eutectic solvents synthesized with glycerol as a hydrogen bond donor had lower removal efficiencies than those synthesized with ethylene glycol, triethylene glycol or 2,2,2-trifluoroacetamide, and the phosphunium-based deep eutectic solvents were more efficient in removing total glycerol than the ammonium-based deep eutectic solvents. The choline chloride:glycerol and MTPB:glycerol deep eutectic solvents were also shown to reduce KOH (around 98%) and water contents in the crude biodiesel based on palm oil below the standard limits [49].

Li et al. [46] extracted unsaturated fatty acid esters (methyl linolenate and linoleate) from soybean-based biodiesel using novel π-complexing sorbents in order to reduce NO_x emissions and to enhance the oxidation stability of the biodiesel. These sorbents were obtained by covalently attaching the imidazolium type of ion liquids onto silica which was followed by coating with silver salts. One of the sorbents ($AgBF_4/SiO_2 \cdot Im^+ \cdot PF_6^-$) exhibited a higher sample capacity and selectivity in extracting 18:3 ester than conventional sorbents. The same group reported the high selectivity of a new adsorbent based on mesoporous silica (i.e. $AgBF_4$/SBA-15 $\cdot$ HPSiOEtIM$^+ \cdot PF_6^-$) for separating polyunsaturated triacylglycerols such as linolenin [51].

Since the biodiesel purification technique using deep eutectic solvents is found to be effective in the removal of glycerol, mono- and diacylglycerols, KOH and water from crude biodiesel, it should be further studied for extension and scale-up of the process.

2.4. Comparison of different crude biodiesel purification methods

Currently, water washing is most widely used in industrial units for the biodiesel production, but there is the increasing interest in crude biodiesel purification by dry washing and membrane separation. Table 2 summarizes the results of comparing different methods for purification of crude biodiesel at laboratory scale. The crude biodiesels were obtained from refined oils, waste cooking oils and waste animal fats using methanol or ethanol in the presence of KOH, NaOH or sodium methoxide as catalysts. Purification efficiencies of wet and dry washing methods have been mainly compared [5,52–60], although vacuum distillation and membrane separation have also been included in two separate comparative studies [61,62]. None of the studies compares the purification efficiency of ionic liquids with that of the traditional methods. Distilled, tap and acidified waters, as well as organic solvents (petroleum ether, *n*-hexane) are used for wet washing, and magnesium silicate (Magnesol), silica, bentonite, activated carbons and ion exchange resins (Amberlite, Purolite, Lewatit) are employed for dry washing. Washing with hot distilled water appears to be the best refining method among the water washing methods. The concluding remarks presented in Table 2 indicate controversial observances on the purification efficiency (refining yield, fuel properties and the fulfillment of prescribed standard limits) of wet and dry washing of crude biodiesels obtained in different production processes. Some studies showed water washing as more efficient than dry washing, while a few others concluded vice versa. Thus, some tests with the produced crude biodiesel using various purification methods and technoeconomic analysis of the overall process will be probably needed to evaluate their real purification efficiency in each specific process of the biodiesel production. The biodiesel purification process of choice should be balanced between the purification efficiency and operational costs.

There are additional difficulties in selecting the proper method for crude biodiesel purification. The effect of basic reactants (especially oily feedstock) on the efficiency of purification methods has been rarely studied. Also, refining yields achieved by various purification methods are scarcely known. Furthermore, there are no data on operational costs of purification methods. An additional obstacle for selecting the best crude biodiesel purification process is the lack of data on pilot and large-scale plants. Therefore, it is difficult to withdraw general conclusion on the purification efficiency of the methods for refining crude biodiesels obtained from different feedstocks and production processes, which could be helpful for selecting the best purification method. Instead, the comparative studies of crude biodiesel purification methods will be separately discussed hereinafter with the emphasis on their main results.

Table 3
A review on biodiesel production and purification methods regarding to oily feedstocks.

Oily feedstock	Biodiesel production process	Purification methods	Operating conditions of purification	Optimal operating conditions of purification	Product properties	Concluding remarks	Reference
Palm oil	NaOH (0.5% of oil), methanol:oil molar ratio: 6:1, 65 °C, 90 min	Adsorption by activated low silica bentonite (0.1–1 M H_2SO_4, 100 °C, 1–12 h); filtration	Adsorbent amount: 1–10% of FAME, 60–200 mesh, 10 min, 200 rpm	Activation by 0.1 M H_2SO_4 during 1 h, particle size 120–200 mesh, amount of 5%		High efficiency in glycerol removal	[26]
	KOH (1% of oil), methanol:oil molar ratio: 6:1, 700 rpm, 60 °C, 60 min	Stepwise washing with water acidified with tannic acid (0.1%) at 60 °C under stirring; drying by evaporation; adsorption by activated palm shell carbon under stirring	Adsorbent amount: 0.01–1 g/25 ml of biodiesel, 1–24 h, 25–60 °C	0.9 g/25 ml of biodiesel, 20 h, 40 °C	KOH: 4.37 mg/kg	Decreases water consumption	[29]
	KOH (1.2% of oil), methanol:oil molar ratio: 6:1, 200 rpm, 60 °C, 60 min	Methanol evaporation under vacuum; separation using ceramic membrane tubes	Membrane pore size: 0.1, 0.2 0.6 μm, transmembrane pressure: 0.05–0.20 MPa, 30–70 °C	Membrane pore size 0.1 μm, 0.15 MPa, 60 °C, permeate flux 300 $L/m^{-2}h^{-1}$	K: 1.4 ± 0.24 ppm, Na: 1.78 ± 0.30 ppm, Ca: 0.81 ± 0.28 ppm, Mg: 0.20 ± 0.11 ppm, FGC: 0.0108 ± 0.0034%	No waste water The use of methanol for cleaning the membrane	[33]
	KOH (1% of oil), 645 rpm, 60 °C, 60 min	Gravitational settling; evaporation (65 °C, 600 mmHg, 45 min); addition of acidified water; membrane separation by using ceramic membrane (0.02 μm)	Transmembrane pressure: 1–3 bar, 30–50 °C, flow rate: 60–150 L/min	2 bar, 40 °C, 150 L/min	ρ (15 °C): 878 kg/m^3, ν (40 °C): 4.91 mm^2/s, FGC: 0.007%, K: 0.297 mg/L, CP: 14 °C, FP: 179 °C, PP: 5 °C	Properties of biodiesel met both ASTM D6751 and EN 14214 standards	[37]
	KOH (1% of oil), methanol:oil molar ratio: 10:1, 400 rpm, 50 °C, 2 h	Gravitational settling; extraction by mixture of choline chloride and glycerol (DES) (170 rpm, 1 h); settling for 2 h	Molar ratios: choline chloride:glycerol: 1:1–1:3, biodiesel:DES 1:1–1:2	Choline chloride:glycerol 1:1, biodiesel:DES ratio 1:1	Glycerol content met the EN 14214 and ASTM D 6751 standard specifications	Biodiesel:DES molar ratio was more important than the DES composition for extraction efficiency	[45]
	KOH (1% of oil), methanol:oil molar ratio: 10:1, 400 rpm, 50 °C, 2 h	Gravitational settling; extraction by two DES with choline chloride and ethylene glycol (HBD1) or 2,2,2-trifluoroacetamide (HBD2) (200 rpm, 1 h); settling for 2 h	Molar ratios: salt:HBD1 1:1.75–1:2.5; salt:HBD2 1:1.5–1:2.5; biodiesel:DES 1:0.75–1:3	Salt:HBD1 1:2.5; Salt:HBD2 1:1.75; biodiesel:DES 1:1		Free glycerol is completely removed	[47]
	KOH (1% of oil), methanol:oil molar ratio: 10:1, 400 rpm, 60 °C, 2 h	Gravitational settling; extraction by DES based on methyl triphenyl phosphunium bromide (MTPB) and glycerol (HBD1), ethylene glycol (HBD2) or triethylene glycol (HBD3) (200 rpm, 1 h); settling for 2 h	Molar ratios: MTPB:HBD1 1:2–1:4; MTPB:HBD2 1:3–1:5; MTPB:HBD3 1:3–1:5	MTPB:HBD2 1:3; MTPB: HBD3 1:4; biodiesel:DES 1:0.75	All DESs reduced the total glycerol below the ASTM standard	All tested DESs reduced the content of mono- and diacylglycerols; the most efficient was HBD3 based DES	[48]
	KOH (1% of oil), methanol:oil molar ratio: 10:1, 400 rpm, 60 °C, 2 h	Gravitational settling; extraction by DESs based on choline chloride and MTPB and HBDs: 2,2,2-trifluoroacetamide, glycerol, ethylene glycol or triethylen glycol (200 rpm, 1 h) settling for 2 h	Molar ratios: choline chloride:HBDs – 1:1–1:2.5; MTPB:HBDs – 1:2–1:5; biodiesel:DES – 1:0.75–1:3	KOH removal (> 99.87%): choline chloride:glycerol 1:3; biodiesel:DES 1:0.75 Water removal (92.02%): choline chloride:2,2,2-trifluoroacetamide 1:2; biodiesel:DES 1:3	All DES reduced the water content below the EN 14214 standard	For KOH removing the most efficient were choline chloride: glycerol and MTPB:glycerol DES	[49]
Crude palm oil	MW two-step process (70 W): 1. H_2SO_4-catalyzed esterification (1% of oil, ethanol:oil molar ratio 6:1, 60 min) 2. KOH-catalyzed ethanolysis (0–2% of oil, ethanol:oil molar ratio 1:1–6:1, 1–10 min)	MW washing with glycerol; ethanol evaporation (80 °C); adsorption with bleaching earth	Glycerol washing: 0–20% of esters, 70 W, 1 min Adsorption: 0–1.4% of esters, stirring, 5 min	Glycerol amount: 10%; bleaching earth 1.2%	ρ (15 °C): 875.3 kg/m^3, ν (40 °C): 5.78 mm^2/s, CP: 7 °C, PP: 4 °C, FP: 178 °C, AV: 0.73 mg KOH/g,EC: 97.4%, AC: 0.016%, WC: 0.03%	Yield: 85% Most of the properties fall within the ASTM standard for methyl ester	[23]

Palm fatty acid distillate	Continuous acid catalyzed esterification: 75 °C, catalyst: H_2SO_4 (1.83% of distillate), methanol:palm fatty acid distillate molar ratio: 8.8:1, 60 min	Neutralization by 3 M NaOH; water washing; drying by evaporation	The amount of 3 M NaOH solution: 2.05–10.24% of FAME phase; 80 °C, 20 min, stirring	10.24% of 3 M NaOH solution	ρ (15 °C): 879 kg/m^3, ν (40 °C): 4.87 mm^2/s, FP: 180 °C, PP: 14 °C, WC: 0.03%, AC: 0.007%, CR: 0.07%, AV: 0.64 mg KOH/g	Most of the properties satisfied the ASTM D6751 standard	[63]
Castor oil	Ethanolysis, catalyst: KOH, NaOH, 400 rpm, 70 °C, 2 h	Stepwise washing with acid water; water washing to neutralize biodiesel; drying with magnesium sulfate	Water temperature: 30 and 70 °C Acid water pH: 2 and 5	pH=2		The amount of wash water was not significantly influenced by water temperature and catalyst type	[14]
Canola oil	Two base catalyzed step process with glycerol removal between steps (each step: 25 °C, catalyst: KOH 0.5% of oil, methanol:oil molar ratio: 3:1, 20 min)	Methanol evaporation; adsorption by silica gel; filtration; drying with sodium sulfate	Adsorption time: 20 min		ρ (30 °C): 875 ± 0.6 kg/m^3, ν (40 °C): 4.23 ± 0.05 mm^2/s, CP: 1–2 °C, PP: −8 to −10 °C, AV: 0.154 ± 0.01 mg KOH/g, IV: 127 g I_2/100 g, K: 227 ppm	Ester yield relative to theoretical yield: 87% Physical and chemical characteristics of biodiesel are similar to diesel fuel	[19]
	NaOH (1% of oil), methanol:oil molar ratio: 6:1, 60 °C, 60 min	Methanol evaporation under vacuum (0.94 bar, 90 °C, 30 min); ultrafiltration by using modified polyacrylonitrile membrane (100 kD cut-off)	25 °C, 552 kPa, addition of water (0.06–0.2%), soap (1%), methanol (1%), soap (1%)+water (0.06%) or soap (1%)+methanol (1%)+ water (0.06%)	Addition of 0.2% water	FGC < 0.14 ppm	Presence of methanol and soap negatively influenced glycerol separation	[35]
	NaOH (1% of oil), methanol:oil molar ratio: 6:1, 60 °C, 60 min	Gravitational settling; membrane separation by using ceramic membrane module consisting of ultrafiltration (0.05 μm, 552 kPa) or microfiltration (0.2 μm, 207 kPa)	0–25 °C	Ultrafiltration membrane, 25 °C, 3 h	FGC: 0.018 ppm	The smaller pore size of the ultrafiltration membrane facilitated glycerol removal	[36]
Rapeseed oil	Two-step process: 1. H_2SO_4-catalyzed esterification (1% of oil, methanol:acid molar ratio: 33:1, 60 °C, 2 h) 2. NaOH-catalyzed methanolysis (0.7–0.9% of oil, methanol:oil molar ratio: 6:1, 60 °C, 1.5 h)	Single water washing under agitation	Water amount: 30–90% of biodiesel, 30–60 °C, 30 min	30% of water and 40 °C	AV: 0.79 mg KOH/g, ν (40 °C): 4.54 mm^2/s, WC: 1053.6 ppm, Na: 28.6 ppm[a], MC: 0.45%[a]	Methanol, Na and glycerol were almost completely removed; the glycerides content was not affected by the washing conditions	[13]
	KOH or NaOH (0.13% of oil), ethanol:oil molar ratio: 4:1, 400 rpm, 40 °C, 24 h	Gravitational settling; extraction by pure quaternary ammonium salt or mixture of quaternary ammonium salt and glycerol	Quaternary ammonium salts: acetylcholine chloride, choline chloride, $ClEtMe_3NCl$, $EtNH_3Cl$, Pr_4NBr	Mixture of choline chloride, $ClEtMe_3NCl$ and $EtNH_3Cl$ with glycerol at the molar ratio of 1:1	For choline chloride–glycerol mixture: glycerol: 0.02%		[44]
Soybean oil	Non-catalytic methanolysis: 280 °C, methanol:oil molar ratio: 15:1–20:1	Distillation of methanol, water and volatile products; glycerol settling; adsorption with activated carbon, impregnated activated carbon, diatomaceous earth or silica gel	Distillation: reboiler 80 °C, condenser 15 °C, 1 h Adsorption: room temperature, adsorbent amount: 0.3–5%, 720 min, stirring	Silica gel, 90 °C, 0.21 bar, 90 min		Methyl ester, glycerides and acid content met EN 14214 standard	[22]
	KOH or NaOH (0.13% of oil), ethanol:oil molar ratio: 4:1, 400 rpm, 40 °C, 24 h	Gravitational settling; extraction by: pure quaternary ammonium salt or mixture of quaternary ammonium salt and glycerol	Quaternary ammonium salts: acetylcholine chloride, choline chloride, $ClEtMe_3NCl$, $EtNH_3Cl$, Pr_4NBr	Mixture of choline chloride, $ClEtMe_3NCl$ and $EtNH_3Cl$ with glycerol at the molar ratio of 1:1	For choline chloride–glycerol mixture: glycerol: 0.06%		[44]
Rice bran oil	In situ esterification catalyzed by H_2SO_4, followed by filtration, washing with methanol and	Adsorption by rice hull ash or silica gel; filtration; evaporation	Adsorbent amount: 1–4 g per 50 ml of FAME-hexane	Silica gel 4 g/50 ml of FAME-hexane solution	EC: 97.4, 92.9 and 91.8%[b], FFA: 2.47, 1.36 and 1.19%[b]	Adsorption efficiency of FFA and FAME increased with increasing the adsorbent dosage	[18]

Table 3 (*continued*)

Oily feedstock	Biodiesel production process	Purification methods	Operating conditions of purification	Optimal operating conditions of purification	Product properties	Concluding remarks	Reference
	water, and extraction with hexane (three times)		solution; 25 °C, 30 min, stirring				
Waste cooking oil	Two-step process: 1. H_2SO_4-catalyzed esterification (1% of oil, methanol:acid molar ratio: 33:1, 60 °C, 2 h) 2. NaOH-catalyzed methanolysis (0.7–0.9% of oil, methanol:oil molar ratio: 6:1, 60 °C, 1.5 h)	Single water washing under agitation for 30 min	Water amount: 30–90% of biodiesel, 30–60 °C, 30 min	30% of water, 40 °C	AV: 0.64 mg KOH/g, ν (40 °C): 4.53 ± 0.03 mm^2/s, WC: 1089.2 ppm, Na: 28.8 ppm[a], MC: 0.43%[a]	Lower water amount and temperature were recommended	[13]
	Non-catalytic methanolysis: 280 °C, methanol:oil molar ratio: 15:1–20:1	Distillation of methanol, water and volatile products; glycerol settling; adsorption with activated carbon, impregnated activated carbon, diatomaceous earth or silica gel	Distillation: reboiler: 80 °C, condenser: 15 °C, 1 h Adsorption: room temperature, adsorbent loading:0.3–5%, 720 min, stirring	Silica gel, 90 °C, 0.21 bar, 90 min		Methyl ester, glycerides and acid content met EN 14214 standard	[22]
Waste fryer grease	Two base catalyzed step process with glycerol removal between steps (each step: KOH 0.75% of oil, methanol:oil molar ratio: 3:1, 25 °C, 20 min)	Methanol evaporation; adsorption by silica gel; filtration; drying with sodium sulfate	Adsorption time: 20 min		ρ (30 °C): 872 ± 1 kg/m^3, ν (40 °C): 4.63 ± 0.1 mm^2/s, CP: 4–5 °C, PP: −1 to −1 °C, AV: 0.194 ± 0.016 mg KOH/g, IV: 98 g I_2/100 g, K: 78 ppm	Ester yield relative to theoretical yield: 58%	[19]
Chicken fat	Non-catalytic methanolysis: 280 °C, methanol:oil molar ratio: 15:1–20:1	Distillation of methanol, water and volatile products; glycerol settling; adsorption with activated carbon, impregnated activated carbon, diatomaceous earth or silica gel	Distillation: reboiler: 80 °C, condenser: 15 °C, 1 h Adsorption: room temperature, adsorbent loading:0.3–5%, 720 min, stirring	Silica gel, 90 °C, 0.21 bar, 90 min		Methyl ester, glycerides and acid content met EN 14214 standard	[22]
Beef tallow	NaOH or NaMeO (0.5–1.5% of oil), methanol:oil molar ratio: 6:1, 65 °C, 20–45 min	Washing (two times) with an equivalent volume of warm water; distillation under vacuum; drying	Distillation under vacuum: 30–80 °C; drying: 80 °C, 10 min			FAME yield: 97–99%	[64]
Pollock oil	NaOH (1% of oil), methanol:oil molar ratio: 6:1, 55 °C, 20–60 min	Adsorption by activated earth; centrifugation	Adsorbent amount: 10% of FAME; 30 °C, 60 min, stirring		ρ (20 °C): 880 ± 10 kg/m^3, ν (25 °C): 0.006 Pa·s, CP: −11 °C, FP: 84 °C, FFA: 0.35 ± 0.03%, WC: 399 ± 1 ppm, FGC: 2.30 ± 0.12 ppm, TC: 969.29 ± 14.08 ppm, Ca: 30.73 ± 3.99 ppm, K: 3.81 ± 0.4 ppm, Na: 2.96 ± 0.9 ppm	Yield 85.6 ± 1% Biodiesel met the ASTM D6751 biodiesel standard	[24]

DES, deep eutectic solvents; HBD, hydrogen-bond donor; MW, microwave assisted; ρ, density; ν, viscosity; FGC, free glycerol content; CP, cloud point; FP, flash point; PP, pour point; EC, esters content; AC, ash content; WC, water content; CR, carbon residue; AV, acid value; IV, iodine value; MC, methanol content; FFA, free fatty acid content; TC, total glycerol content.

[a] Simulated value.

[b] For 2, 5 and 10 vol% of crude FAME in *n*-hexane, respectively.

Karaosmanoğlu et al. [52] used three washing processes for refining crude biodiesel obtained from rapeseed oil: hot distilled water washing, dissolution of crude biodiesel in petroleum ether followed by water washing and neutralization of crude biodiesel with sulfuric acid (1:1). The biodiesels obtained by different washings had approximately the same composition of methyl esters. However, the highest refining yield of 84.2% and the lowest water content and acid value was achieved by the distilled water washing at 50 °C.

Canoira et al. [53] compared wet and dry washings of crude biodiesel obtained from a mixture of animal fat and soybean oil. The former process resulted in a better biodiesel yield, while all other parameters were almost identical. However, the oxidative stability, the total contamination and the sulfur content were slightly better for the dry washing although out of the prescribed limits for both methods.

Berrios and Skelton [5] compared water washing, magnesium silicate (Magnesol) and ion-exchange resins (BD10 Dry and Purolite PD206) for the removal of glycerol, methanol and soap from two crude biodiesels obtained from refined vegetable and waste cooking oils. Despite different feedstocks used for producing the biodiesels tested, the purification processes resulted in similar effects. Only the water washing process reduced methanol and free glycerol concentrations below to those prescribed by the standard, but it did not affect the concentrations of acylglycerols like other two processes. Soap removal efficiencies of wet washing and ion-exchange treatment were equal to each other and significantly better than that of the Magnesol treatment. Washing by tap water at room temperature and water-to-biodiesel ratio of 0.5:1 gave the best glycerol removal below the prescribed limit within 10 min. Magnesol had a better effect on the methanol removal than the resins, but both adsorbents did not reduce the methanol concentration below the standard limit. The resin treatment reduced the free glycerol concentration below the standard limit, but the methanol removal capacity of both resins was low. None of the tested processes significantly affected the acid value, oxidation stability and concentrations of acylglycerols and water.

Predojevic [54] examined the purification of the biodiesel originating from waste cooking oils by hot distilled water washing, phosphoric acid washing and silica gel adsorption. The first method yielded the lowest yield (89%), while the treatments with phosphoric acid and silica gel resulted in a somewhat higher yield (92%). The final biodiesels satisfied the criteria prescribed with the biodiesel fuel standards with respect to density, viscosity, acidity (except that obtained from the waste cooking oil having the initial acid value of 3 mg KOH/g), iodine value and purity.

Mata et al. [55] investigated two purification procedures for crude biodiesels from beef tallow, pork lard and chicken fat. The first method involved hot distilled water washing while the second one employed a cationic exchange resin. The methyl esters content of all biodiesels was below the prescribed standard limit of 96.5%. Water washing gave better results regarding water and group I metal (Na+K) content, while dry washing reduced the acidity and viscosity of biodiesel. Density, flash point and cold filter plugging point of the biodiesels did not depend on the purification method.

Mendow et al. [56] studied three different methods for purification of a mixture of methyl and ethyl esters. Two methods consisted of two-step washing with neutral water or 5% of hydrochloric acid (the first step) followed by water saturated with carbon dioxide water (the second step) or only water saturated with carbon dioxide (in both steps). The third method was an adsorption by passing crude biodiesel through a column with an Amberlite resin. All three processes were effective in eliminating soap and glycerol, but only the method involving neutral water in the first washing step removed the soaps without formation of free fatty acids and resulted in the acidity below the prescribed limit.

Berrios et al. [57] examined the purification efficiency of wet washing (with distilled water, tap water or glycerol), adsorption (Magnesol or bentonite) and ion exchange (Lewatit GF 202). All methods effectively removed methanol, glycerol and soap, but they did not affect density, viscosity, as well as methyl ester and the acylglycerols content. The same results were observed when using distilled and tap water. Soap and methanol were removed with glycerol washing to the same extent as with water washing. Glycerol was the only solvent which positively affected the water content, but it negatively influenced the free glycerol content.

Faccini et al. [58] compared the performances of various adsorbents, such as Magnesol, silica (inorganic matrices), Amberlite BD10 DRY and Purolite PD 206 (organic resins), with that of hot acid/water washing for purification of soybean-oil-based biodiesel. Magnesol and silica had the better efficiency than the organic resins, especially for removing soap, free and total glycerol and potassium. The purification results of the adsorption process using the inorganic matrices were comparable with those of the combined acid/water washing.

Recently, some research teams have used agricultural wastes, such as rice husk [59] or tea waste [60], to produce effective adsorbents for crude biodiesel purification, which could be either used as a soil corrective or regenerated for reusing as an adsorbent. Manique et al. [59] compared the efficiency of dry and wet washing of the biodiesel from waste frying oil. Rice husk ash and the commercial adsorbent Magnesol were used for dry washing, and the phosphoric acid solution (1%) was employed for wet washing. In the concentration of 4%, rice husk ash was very efficient in removing impurities from crude biodiesel such as glycerol, acylglycerols, methanol, water and potassium. The performance of rice husk ash was comparable to those of the acid solution and the commercial adsorbent. Fadhil et al. [60] purified the crude biodiesel produced from waste cooking oil using activated carbons obtained from the spent tea waste. For comparison, silica gel and water washing were also employed. The use of activated carbons resulted in higher ester yields and better fuel properties compared to the other two methods. The spent activated carbons were regenerated and reused for purifying the crude biodiesel. The purified biodiesel met the specifications of the biodiesel ASTM standards.

Pighinelli et al. [61] employed distillation under vacuum (680 mmHg) to purify the crude biodiesel produced from sunflower oil. This method showed the purified biodiesel yield of 92.3% that was higher than those achieved by wet and dry washing (84.2 and 84.6%, respectively). The purified biodiesel met most of the specified requirements, except water and free glycerol contents.

He et al. [62] compared the membrane separation method using hollow fiber membranes with traditional purification methods. Biodiesel of a high purity (97.5%) was obtained by using traditional methods, but with high purification losses because of serious emulsification. The use of hollow fiber membrane prevented emulsification, reduced the purification loss and resulted in the biodiesel purity of 99%. The polysulfone membrane was selected as more suitable than the polyacrylonitrile one. Some product properties (density, viscosity, water content and acid value) were below the ASTM standard limits.

2.5. Comparison of crude biodiesel purification methods regarding oily feedstocks

Crude biodiesels used in purification studies originate from a variety of feedstocks, such as vegetable oils (palm, soybean, rapeseed, canola and castor oil), rice bran oil, palm fatty acid distillate,

animal fats (chicken fat and beef tallow), pollock oil, waste cooking oil and waste fryer grease. However, the systematic studies on the combined effect of the purification method and the type of feedstock on the fuel properties of the final product have been rarely conducted. Only two studies deal with wet and dry washing of crude biodiesels obtained from different sources of triacylglycerols (refined edible oil and waste cooking oil [5] and from beef tallow, pork lard and chicken fat [55]). Despite different feedstocks, both purification processes resulted in similar effects: the product biodiesels had approximately the same composition [5] and the fuel properties evaluated [55], but none of them satisfied the prescribed standard completely.

In an attempt to assess the impact of oily feedstock on the effectiveness of various purification methods, we summarize the previous studies on refining crude biodiesels obtained from different raw materials in Table 3. Since the FAME synthesis method influences the crude biodiesel properties and the efficiency of purification process [4], the reaction conditions applied in the biodiesel production are also included in Table 3. As it can be concluded from Table 3, most of the studies refer to the crude biodiesel obtained from palm oil [23,26,29,33,37,45,47–49]. Refining yields have been rarely reported in the considered studies. The efficiency of each purification method is assessed according to the properties of the purified biodiesel product. The specific advantages and disadvantages of each method are also emphasized in Table 3. Most of the properties of purified biodiesels are not reported in different studies, creating a difficulty in comparing the methods employed for refining crude palm oil biodiesel and selecting the best one. However, it is evident from the presented data that the efficiency of removing various impurities from crude palm oil biodiesel varies among the purification methods employed.

Various purification methods have been applied in palm oil biodiesel purification, such as adsorption [23,26,29], membrane separation [33,37] and ionic liquid treatment [45,47–49]. The adsorption method using activated low silica bentonite showed a high efficiency in free glycerol removal [26]. Activated palm shell carbon used after stepwise washing with hot acidified water reduced KOH amount and water consumption [29]. Also, the combined washing with pure glycerol and adsorption with bleaching earth resulted in the 85% yield of the biodiesel product satisfying the ASTM standard [23]. The best results in palm oil biodiesel purification were obtained by using the membrane separation technology [33,37]. The biodiesel fulfilling the both ASTM D6751 and EN 14214 standards was obtained by membrane extraction with ceramic membrane [37]. Acidified water was also included in the refining process to improve the retention of biodiesel water-soluble impurities in the membrane system. The use of deep eutectic solvents was successful in removing glycerol [45,47,48] and water [49] and in reducing the content of mono- and diacylglycerols [48]. However, other biodiesel properties were not tested.

In the case of refining crude biodiesels from other oily feedstocks, only the adsorption with silica gel [19] and activated earth [24] produced the final product from canola and Pollock oils, respectively satisfying the standard limits. The yield of canola oil biodiesel (relative to the theoretical yield) was 87%, and its physical and chemical characteristics were similar to those of diesel fuel [19]. The yield of the biodiesel obtained from pollock oil was 85.6% [24].

3. Conclusions

For commercial application, the ester product of alkali-catalyzed transesterification should be refined after glycerol separation by settling in order to fulfill the biodiesel standard specifications. After neutralization and methanol removal this crude biodiesel is further cleaned by either one of the following methods: wet washing, dry washing, membrane extraction or using ion liquids. Each method has its advantages and disadvantages, which should be carefully analyzed when choosing the proper one for refining crude biodiesel.

Ensuring that the final product meets the biodiesel standard specifications, water washing has been the most frequently used process, although it suffered from several drawbacks including the water cost, possible emulsion formation, drying of biodiesel and wastewater treatment. Dry washing appears to be a promising method for refining crude biodiesel, but a solution for the generated solid waste should be found. Membrane technology circumvents the need for traditional water washing of crude biodiesel and might be a future choice for crude biodiesel refining. The membrane extraction results in avoiding the emulsification which is characteristic for water washing and in reducing the environmental problem of disposal (little or no wastewater generation) but it increases the final biodiesel production cost. Further research should be performed in order to make use of ionic liquids for crude biodiesel refining. The main challenges are to reduce their production cost, to develop easy methods for their recovery and to develop effective methods for their recycling.

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